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(54) [Title of the Invention] MAGNETIC THIN FILM

(57) [Abstract]
[Problem to be Solved] To provide a magnetic thin film which simultaneously realizes a high saturation magnetic flux density and a high resistivity, reduces losses caused by eddy currents or ferromagnetic resonance, and shows a high permeability even at a high frequency.
[Solving Means] According to the present invention, a soft magnetic thin film in which a phase of fine ferromagnetic metal grains having an average grain size of 20 nm or less and a phase of a high resistivity ferromagnetic insulator exist in a granular structure and which shows a high permeability of 300 or more at a high frequency of, for example, 500 MHz or more, and, at the same time, has a high saturation magnetic flux density of 1.3 T or more is provided. In particular, the ferromagnetic metal phase contains at least one kind of iron and cobalt as a main constituent element, and the ferromagnetic insulating phase is an oxide containing iron and oxygen as main constituent elements, does not substantially form a solid solution with the ferromagnetic metal, and contains a nonmagnetic metal element (for example, one or more kinds of elements selected from Au, Ag, and Cu) which is difficult to be oxidized than the ferromagnetic metal at a ratio of 20 at% or less. Thereby, the foregoing soft magnetic thin film can be provided.

[Claims]

[Claim 1] A magnetic thin film, comprising:

a ferromagnetic metal phase; and

a ferromagnetic insulating phase having resistivity of 1000 μΩcm or more,

wherein an average grain size of metal grains constituting the ferromagnetic metal phase is 20 nm or less.

[Claim 2] The magnetic thin film according to claim 1, wherein an average grain size of metal grains constituting the ferromagnetic metal phase is 10 nm or less.

[Claim 3] The magnetic thin film according to claim 1 or 2, wherein the ferromagnetic metal phase contains at least one kind of iron and cobalt as a main constituent element, and the ferromagnetic insulating phase is an oxide of which main constituent elements are iron and oxygen.

[Claim 4] The magnetic thin film according to any one of claims 1 to 3, wherein at least one kind of nonmagnetic metal elements that do not substantially form a solid solution with the ferromagnetic metal and are difficult to be oxidized than the ferromagnetic metal is contained at a ratio of 20 at% or less.

[Claim 5] The magnetic thin film according to any one of claims 1 to 4, wherein the nonmagnetic metal elements that do not substantially form a solid solution with the ferromagnetic metal and are difficult to be oxidized than the ferromagnetic metal are Au, Ag and Cu.

[Detailed Description of the Invention]

[0001]

[Industrial field of application] The present invention relates to a magnetic thin film, in particular, a soft magnetic thin film for magnetic heads, thin film inductors, thin film transformers, thin film magnetic filters and the like, which are suitably used in high frequency.

[0002]

[Prior Art] In recent years, as the miniaturization of electronic devices is forwarded, high frequency of various kinds of electronic devices and magnetic devices is promoted. For example, in a magnetic head, the operating frequency thereof is expected to be heightened in near future from present several tens MHz to several hundreds MHz or more. In addition thereto, also in micro-magnetic devices such as thin film inductors,

transformers and the like and noise filters, a shift to high frequency is in demand. However, a conventional magnetic metal thin film of such as NiFe alloy or the like has low resistivity ρ to result in causing large eddy current loss to lower the permeability at high frequency; accordingly, there was a problem that the conventional magnetic metal thin film cannot deal with high frequency devices like this. Also from the technical background like this, a soft magnetic thin film capable of dealing with high frequency of several hundreds MHz or more is being demanded to be realized.

[0003] In general, a cause that limits the frequency characteristics of a magnetic material is loss owing to eddy current and magnetic resonance. Firstly, an eddy-current loss-frequency can be decreased by thinning a film of magnetic material and by making the resistivity of the magnetic material higher. The ferromagnetic resonance frequency can be shifted toward a higher frequency side by making the saturation magnetization larger and by imparting a larger anisotropic magnetic field. That is, a magnetic material exhibiting excellent characteristics in a high frequency region is a thin film body having high resistivity and high saturation magnetic flux density.

[0004] As a soft magnetic thin film having high resistivity, a soft magnetic thin film having a granular structure where a ferromagnetic metal phase and a nonmagnetic insulating phase exist in a phase-separated state has been known. The "granular structure" here represents a structure where a ferromagnetic metal phase is present dispersed in an insulating phase as fine grains.

[0005] For example, in Japanese Patent Publication No. 4-26105, a soft magnetic thin film represented by "Fe-M-O" (M represents one or more kinds of elements selected from 3A group elements and 4A group elements) is disclosed.

[0006] Furthermore, in Japanese Patent Publication No. 4-62806, a soft magnetic thin film represented by "Co-M-O" (M represents one or more kinds of elements selected from 3A group elements, 4A group elements and 5A group elements) is disclosed.

[0007] The soft magnetic thin films having the granular structure are constituted of a ferromagnetic metal element such as Fe or Co, an element M more readily bonding with oxygen than the ferromagnetic metal element, and oxygen.

[0008] According to the granular structure where the ferromagnetic phase and the nonmagnetic oxide insulating phase are present in a phase-separated state, high resistivity can be realized. That is, IEE, Magnetic Study Group, MAG-96-158 reports that, in "Co-M-O" (Ge, Sn, Si, Al as M) system granular structure films, depending on the heat of formation (that is, a degree of easy oxidizability of M) of M oxides, the resulting film structures are different, that is, the larger the difference between heats of formation of cobalt oxide and M oxide is, the more readily the granular structure film is formed. Furthermore, it is also reported that the "Co-Al-O" system granular structure film, though not clear as to the reason, when Pd is added, can obtain a large anisotropic magnetic field and excellent soft magnetic property.

[0009] In the soft magnetic thin film having the granular structure where the ferromagnetic phase and the nonmagnetic oxide insulating phase are present in a phase-separated state, it is necessary to increase a ratio of the insulating phase in the film to obtain high resistivity. However, since the insulating phase is nonmagnetic, there is a problem that when a ratio thereof is increased, the saturation magnetic flux density decreases. That is, there is a problem that conflicting relationship exists between the high saturation density and the high resistivity.

[0010] On the other hand, in Japanese Unexamined Patent Application Publication No. 6-251939, as a thin film having a ferromagnetic metal phase and a ferromagnetic high resistivity phase, a soft magnetic thin film made of two phases of αFe and Fe_4N is disclosed. Here, Fe_4N is a ferromagnetic body having high saturation magnetic flux density such as 1.6 T, and, αFe occupies 20 to 60% of an entire volume; accordingly, a thin film having high saturation magnetic flux density such high as 1.78 T to 1.91 T is prepared. However, since the resistivity of the Fe_4N is not high, there was a problem that the resistivity of the thin film as a whole is only about 100 $\mu\Omega$cm at best. Although the resistivity of Fe_4N is not specifically disclosed, in some cases, Fe_4N occupies 60% of an entire volume; accordingly, the resistivity is assumed to be 200 to 300 $\mu\Omega$cm or less.

[0011]

[Problems to be Solved by the Invention] The present invention was carried out to solve the problems found in the

conventional technology and intends to provide a magnetic thin film that simultaneously realizes high saturation magnetic flux density and high resistivity, reduces losses owing to eddy current and ferromagnetic resonance and shows high permeability also in high frequency.

[0012]

[Means for Solving the Problems] After studying hard to solve the aforementioned problems, the present inventors came to find magnetic thin films described below. That is,

(1) a magnetic thin film in which a ferromagnetic metal phase and a ferromagnetic insulating phase having resistivity of 1000 μΩcm or more are present, and an average grain size of metal grains constituting the ferromagnetic metal phase is 20 nm or less.

[0013] (2) The magnetic thin film according to (1), wherein an average grain size of metal grains constituting the ferromagnetic metal phase is 10 nm or less.

[0014] (3) The magnetic thin film according to (1) or (2), wherein the ferromagnetic metal phase contains at least one kind of iron and cobalt as a main constituent element, and the ferromagnetic insulating phase is an oxide of which main constituent elements are iron and oxygen.

[0015] (4) The magnetic thin film according to any of (1) to (3), wherein at least one kind of nonmagnetic metal elements that do not substantially form a solid solution with the ferromagnetic metal and are difficult to be oxidized than the ferromagnetic metal is contained at a ratio of 20 at% or less.

[0016] (5) The magnetic thin film according to any of (1) to (4), wherein the nonmagnetic metal elements that do not substantially form a solid solution with the ferromagnetic metal and are difficult to be oxidized than the ferromagnetic metal are Au, Ag and Cu.

[0017]

[Action] According to the present invention, by letting a ferromagnetic metal phase having an average grain size of metal grains of 20 nm or less and a ferromagnetic insulating phase having high resistivity exist in a granular structure, a soft magnetic thin film that exhibits high permeability of 300 or more in a high frequency of, for example, 500 MHz or more, and, in addition thereto, has high saturation magnetic flux density of 1.3 T or more can be provided. In more detail, when the

ferromagnetic metal phase is formed with at least one kind of iron and cobalt as a main constituent element, the ferromagnetic insulating phase is formed of an oxide formed with iron and oxygen as main constituent elements, and a nonmagnetic metal element (at least one kind of, for example, Au, Ag and Cu) that does not substantially form a solid solution with the ferromagnetic metal and is difficult to be oxidized than the ferromagnetic metal is contained at a ratio of 20 at% or less, the soft magnetic thin film according to the present invention can be obtained.

[0018]

[Embodiments of the Invention] The magnetic thin film according to the present invention has a granular structure and can be obtained by letting a predetermined ferromagnetic metal phase and a corresponding ferromagnetic insulating phase exist in a phase-separated state. In more detail, the magnetic thin film is constituted by letting a ferromagnetic metal phase and a ferromagnetic insulating phase having resistivity of 1000 μΩcm or more exist, and an average grain size of metal grains constituting the ferromagnetic metal phase is made 20 nm or less.

[0019] In more detail, when a ferromagnetic metal phase of which main component is, for example, iron and a ferromagnetic insulating phase made of an iron oxide phase are allowed to exist in a phase-separated state, a magnetic thin film according to the present invention is constituted. That is, a granular structure suitable for obtaining soft magnetic characteristics can be obtained by dispersing a ferromagnetic metal phase made of very fine metal grains in a ferromagnetic insulating phase. When such the granular structure is formed, the ferromagnetic metal phase is isolated by the ferromagnetic insulating phase, resulting in exhibiting high resistivity. Furthermore, also the insulating phase here has a ferromagnetic property; accordingly, high saturation magnetic flux density is exhibited. Thus, the magnetic thin film according to the present invention exhibits excellent soft magnetic characteristics and can simultaneously realize high saturation magnetic flux density and high resistivity which have been considered to be incompatible.

[0020] As a metal constituting the ferromagnetic metal phase, in addition to the iron illustrated above, a simple metal

of cobalt and alloys thereof can be selected and used. Furthermore, also ferromagnetic metals containing the iron or cobalt simple metal or alloys thereof as main constituent elements and containing other elements described below can be used. Here, an average grain size of metal grains constituting the ferromagnetic metal phase is preferably set to 20 nm or less (more preferably to 10 nm or less). When the average grain size is larger than the above-mentioned value (that is, 20 nm), the soft magnetic characteristics are deteriorated because of the crystalline magnetic anisotropy. The value of the average grain size here indicates a value calculated from a half-value width obtained by X-ray diffractometry and a value obtained as the result of observation with a transmission electron microscope.

[0021] As a material constituting the ferromagnetic insulating phase used in the present invention, a material having the resistivity of 1000 $\mu\Omega$cm or more is selected and used. When the resistivity thereof is lower than 1000 $\mu\Omega$cm, the resistivity of the thin film as a whole becomes low to result in deteriorating the high frequency characteristics.

[0022] As a material constituting the ferromagnetic insulating phase, for example, γFe_2O_3 that is an oxide of iron can be used. However, as the ferromagnetic insulating phase constituting the magnetic thin film according to the present invention, not only a single phase γFe_2O_3, but also a non-equilibrium "Fe-O" system where an iron oxide phase is locally contained may be used. Furthermore, other ferromagnetic insulators, for example, spinel ferrites such as Fe_3O_4, $ZnFe_2O_4$, $MgFe_2O_4$ and the like may be used to constitute.

[0023] Furthermore, in the magnetic thin film according to the present invention, at least one kind of nonmagnetic metal elements that do not substantially form a solid solution with the corresponding ferromagnetic metal and are more difficult to be oxidized than the ferromagnetic metal is contained desirably at a ratio of 20 at% or less.

[0024] Here, "do not substantially form a solid solution with the ferromagnetic metal" means to include, other than a case where a solid solution is not at all formed, also a case where a solid solubility limit is such low as 15 at% or less. For example, in the case of Cu, a solid solution is formed with a limit of 1.8% with iron and with limits of 10 to 12% with cobalt.

Including the case like this, the above expression was taken.

[0025] The nonmagnetic metal element that does not substantially form a solid solution with the corresponding ferromagnetic metal and is more difficult to be oxidized than the ferromagnetic metal is effectively added to make the ferromagnetic metal phase finer to generate a granular structure suitable for realizing the soft magnetic characteristics. This is because the soft magnetic characteristics are based on a nano scale granular structure (that is, fine structure), and, when the nonmagnetic metal element is added, owing to precipitation thereof, crystal grains of the ferromagnetic metal phase are inhibited from becoming coarse. Furthermore, when the nonmagnetic metal element is added, in addition to lowering the saturation magnetic flux density, the resistivity also is lowered; accordingly, an addition amount thereof is preferably set to 20 at% or less. When the nonmagnetic metal element is added exceeding the limit thereof, not only high saturation magnetic flux density is not obtained but also the resistivity is lowered. As the nonmagnetic metal element, although a simple metal element can be selected from a plurality of kinds of target metal elements, also two kinds or more thereof may be selected as addition elements.

[0026] As effective nonmagnetic metal elements for obtaining, by not allowing to substantially form a solid solution with the ferromagnetic metal mainly made of iron or cobalt, a granular structure suitable for making the ferromagnetic metal phase finer and realizing soft magnetic characteristics, Au, Ag and Cu can be cited.

[0027] The soft magnetic thin film according to the present invention can be produced by applying, for example, a reactive sputtering method or a composite target method. In the former reactive sputtering method, the soft magnetic thin film is produced by a sputter deposition using a ferromagnetic metal as a target in an atmosphere containing oxygen. The target at this time may be either a simple metal target of iron or cobalt or an alloy target containing at least one of these or a composite target obtained by combining with the ferromagnetic metal. Furthermore, a composite target in a form where the nonmagnetic metal element is further combined may be used.

[0028] On the other hand, in the latter composite target

method where the ferromagnetic metal and the ferromagnetic oxide are combined, a soft magnetic thin film according to the present invention is produced by a sputter deposition in a pure Ar atmosphere using a composite target obtained by combining a target of a simple metal of iron or cobalt or an alloy thereof, or a composite target where the above-mentioned nonmagnetic metal element is further combined. The sputter deposition here can be carried out also in a mixed gas atmosphere containing oxygen.

[0029] The sputtering method applicable in the sputter deposition is not particularly restricted to, other than an rf sputtering method, an ion beam sputtering method and the like. In order to promote a reaction during deposition, a substrate on which the soft magnetic thin film is generated can be subjected also to required heating. When the substrate is heated, low temperature heating at 200°C or less is desirable from fear of oxygen diffusion.

[0030] The soft magnetic thin film according to the present invention is desirably deposited in a predetermined magnetic field to impart an anisotropic magnetic field Hk. Other than the above, after depositing in a nonmagnetic field, the heat treatment can be applied in a static magnetic field to impart the Hk.

[0031] Furthermore, the soft magnetic thin film according to the present invention exhibits the soft magnetic characteristics also in a state as deposited. Furthermore, an appropriate heat treatment also may be applied in order to improve the soft magnetic characteristics. In this case, since oxygen in the ferromagnetic oxide phase constituted of, for example, iron oxide may diffuse in the ferromagnetic metal phase, the heat treatment is desirably applied at a temperature of 300°C or less. When oxygen diffuses by heat treating at a high temperature exceeding the temperature, the granular structure is destroyed, and thereby excellent soft magnetic characteristics cannot be exhibited. Furthermore, according to the oxygen diffusion, the saturation magnetic flux density and the resistivity may be as well deteriorated.

[0032]

[Examples] Hereinafter, the present invention will be further described with reference to Examples and Comparative Examples of the present invention.

[0033] Specimens were prepared by the use of an rf magnetron sputtering system.

[0034] As the substrate, a 0.5 mm thick glass substrate (product No.: 7059, manufactured by Corning Incorporated) and a glassy carbon substrate were used while indirectly cooling with water.

[0035] As the target, composite targets were prepared by combining, as shown in [Table 1], 0 to 15% by area of a γFe_2O_3 chip, a Fe-B (80: 20 at%) chip, or nonmagnetic metal chips of Au (gold) and V (vanadium) to a pure iron or pure cobalt target having a diameter of 100 mm.

[0036] Here, Au in Examples is added as a nonmagnetic metal that does not substantially form a solid solution with iron and cobalt.

[0037] Furthermore, V in Comparative Examples is added as a nonmagnetic metal that forms a solid solution with iron.

[0038] The resistivity of an Fe-B (80: 20 at%) chip was 300 $\mu\Omega$cm.

[0039] On the other hand, the resistivity of a γ Fe_2O_3 chip was 5000 $\mu\Omega$cm or more and an accurate numerical value thereof could not be measured.

[0040] Furthermore, pure Ar was used as a sputtering atmosphere.

[0041] In a part of Examples (Examples 6 and 7), specimens were prepared according to a reactive sputtering method where, without using the ferromagnetic oxide chip, a (argon + oxygen) mixed gas containing oxygen at partial pressure of 2% in a sputtering atmosphere was used.

[0042] In order to impart uniaxial magnetic anisotropy to a thin film specimen, a magnetic field of 250 Oe was applied during deposition in parallel with a substrate surface with a permanent magnet. A deposition rate thereof was set to about 2 to 40 nm/sec, and a film thickness was set to about 100 nm for use in composition analysis and to 1 μm for use in composition analysis by EPMA described below and for use in evaluation of the resistivity and magnetic properties.

[0043] The soft magnetic thin films were evaluated in a state as deposited according to measurement methods described below.

[0044] (1) A composition analysis was performed by a Rutherford back-scattering method (RBS) and with an X-ray

microanalyzer (EPMA).

[0045] (2) The resistivity ρ was measured by a direct current four terminal method.

[0046] (3) The saturation magnetic flux density Bs and coercive force Hc were measured with a vibrating sample magnetometer (VSM).

[0047] (4) The permeability μ was measured according to a parallel line method at 500 MHz.

[0048] (5) Crystal grain sizes D were obtained by observing with a transmission electron microscope (TEM) and by applying a Sheller's equation from X-ray diffractometry (XRD).

[0049] The evaluation results are as shown in "Table 2". In Example 1 of "Table 2", for example, "Fe-O8" represents a composition ratio where O is 8 at% and the balance is Fe. In also other Examples and Comparative Examples, the same is applied.

[0050] From above-mentioned results, effects of the present invention are obvious. That is, as obvious by comparing Examples 1 to 9 with Comparative Examples 10 to 16 in "Table 2", the resistivity ρ and the saturation magnetic flux density Bs in each of Examples are simultaneously improved and high permeability μ is obtained.

[0051] According to Examples of the present invention, a magnetic thin film that is less in loss and high in permeability μ also at high frequency can be obtained.

[0052]

[Table 1]

試料番号 (Specimen No.)		ターゲット (Target)	γFe2O3	Fe-B	非磁性金属 (Nonmagnetic Metal)	備考 (Remarks)
1	実施例	純鉄	10	0	0	
2	実施例	純鉄	15	0	0	
3	実施例	純鉄	10	0	Au:0.5	
4	実施例	純鉄	10	0	Au:1.5	
5	実施例	純鉄	10	0	Au:10	
6	実施例	純鉄	0	0	0	反応性スパッタ (Reactive sputtering)
7	実施例	純鉄	0	0	Au:10	反応性スパッタ (Reactive sputtering)
8	実施例	純コバルト	10	0	0	
9	実施例	純コバルト	10	0	Au:1.5	
10	比較例	純鉄	0	0	0	
11	比較例	純鉄	10	0	Au:15	
12	比較例	純鉄	5	0	0	
13	比較例	純鉄	0	20	0	
14	比較例	純鉄	10	0	V:20	
15	比較例	純コバルト	0	0	0	
16	比較例	純コバルト	0	20	0	

(Note) An area ratio of a chip on a target having a diameter of 100 mm is represented in terms of %.

Specimen Nos.1-9: Examples
Specimen Nos.10-16: Comparative examples
Target of Specimen Nos.1-7, 10-14: Pure iron
Target of Specimen Nos.8-9, 15-16: Pure cobalt

[0053]

[Table 2]

Film Composition at%

Specimen No.

試料番号		膜組成 at%	Bs T	Hc Oe	ρ μΩcm	μ —	D nm
1	実施例	Fe−O8	1.7	1.9	750	550	9
2	実施例	Fe−O12	1.5	1.2	980	650	8
3	実施例	Fe−O8 −Au1	1.6	0.8	740	850	5
4	実施例	Fe−O8 −Au3	1.5	0.5	650	750	5
5	実施例	Fe−O8 −Au12	1.4	0.9	500	550	4
6	実施例	Fe−O10	1.6	1.5	600	520	7
7	実施例	Fe−O12−Au8	1.3	0.9	550	880	4
8	実施例	Co−Fe5−O8	1.4	1.1	680	600	8
9	実施例	Co−Fe5−O8−Au3	1.3	0.9	600	650	4
10	比較例	Fe	2.1	4.2	15	40	45
11	比較例	Fe−O8−Au22	0.8	26	280	30	4
12	比較例	Fe−O8	1.8	12	160	50	32
13	比較例	Fe−B5	1.8	5.4	80	70	25
14	比較例	Fe−O9−V23	0.9	32	290	50	31
15	比較例	Co	1.6	4.8	15	30	42
16	比較例	Co−Fe20−B5	1.7	3.2	65	120	27

Specimen Nos.1-9: Examples

Specimen Nos.10-16: Comparative examples

[0054]

[Effects of the Invention] As understood from the detailed description above, according to the present invention, a magnetic thin film that simultaneously realizes a high saturation magnetic flux density and a high resistivity, reduces losses caused by eddy currents or ferromagnetic resonance, and exhibits a high permeability also at a high frequency can be obtained.